AD-A042 449 PENNSYLVANIA STATE UNIV UNIVERSITY PARK DEPT OF CHEMISTRY F/G 7/3

SYNTHESIS OF ALKYL AND ARYL PHOSPHAZENE HIGH POLYMERS. (U)

JUL 77 H R ALLCOCK, D B PATTERSON, T L EVANS N00014-75-C-0685

UNCLASSIFIED TR-77-1 NL

| OF |

AD
A042449

END

DATE FILMED

8-77

DDC

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

12

1. REPORT NUMBER Technical Report No. 77-1	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER 9
4. TITLE (and Subtitle) 6 Synthesis of Alkyl and Aryl Phosphazene High Polymers.		5. TYPE OF REPORT & PERIOD COVERED Interim Technical Report.
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) 10 Harry R. Allcock, Dennis B. Patterson and Thomas L. Evans		8. CONTRACT OR GRANT NUMBER(s) 15 N00014-75-C-0685
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Chemistry The Pennsylvania State University University Park, Pa. 16802		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR 356-577
11. CONTROLLING OFFICE NAME AND ADDRESS Department of the Navy Office of Naval Research Arlington, Virginia 22217	11 28	12. REPORT DATE July 28, 1977
		13. NUMBER OF PAGES Six
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) 14 TR-77-1 12 8p.		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Distribution unlimited; approved for publication

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

Accepted for publication in the Journal of the American Chemical Society

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Polymers, phosphazene polymers, organometallic reagents, carbon-phosphorus bonds, alkyl groups, aryl groups, poly(difluorophosphazenes), high pressure polymerization, crosslinking, chain cleavage, thermal stability.

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The first stable, high molecular weight phosphazene polymers that contain alkyl- or aryl- groups bonded directly to phosphorus have been synthesized by the interaction of organolithium or dialkylmagnesium reagents with poly-(difluorophosphazene). The polymers are elastomers or tough, flexible, film-forming materials.

OFFICE OF NAVAL RESEARCH

Contract N00014-75-C-0685

Task No. 356-577

TECHNICAL REPORT NO. 77-1

Synthesis of Alkyl and Aryl Phosphazene High Polymers

by

Harry R. Allcock*, Dennis B. Patterson, and Thomas L. Evans

Prepared for Publication

in the

Journal of the American Chemical Society

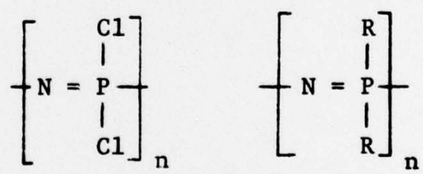
Department of Chemistry
The Pennsylvania State University
University Park, Pennsylvania 16802

July 28, 1977

Synthesis of Alkyl and Aryl Phosphazene High Polymers

Sir:

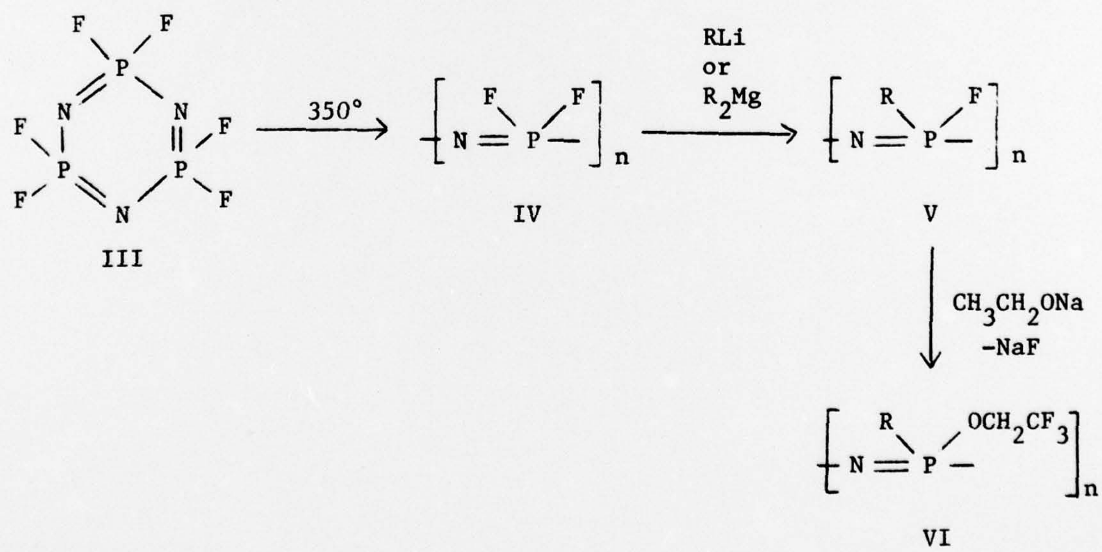
Earlier, we reported the first syntheses of stable, high molecular weight poly(organophosphazenes) of formula $[NP(OR)_2]_n$, $[NP(NHR_2]_n$, and $[NP(NR_2)_2]_n$[1-3] by the interaction of poly(dichlorophosphazene) (I) with alkoxides, aryloxides, or amines. Since that time more than 70 different macromolecules based on these structures have been prepared in different laboratories.[4] These species now comprise a new class of high polymers with unusual fundamental and technological properties. However, all these polymers possess organic side groups bonded to phosphorus through oxygen or nitrogen and, for this reason, reaction pathways exist that permit depolymerization or decomposition at temperatures above 200°. It was anticipated that a new range of phosphazene polymers, perhaps with higher thermal stabilities and unique physical properties, might be accessible if alkyl or aryl groups could be bonded directly to phosphorus through carbon-phosphorus bonds (II).



I II

A few earlier attempts had been made to achieve this end. Polymer I had been allowed to react with Grignard or organolithium reagents,[5,6] but the elemental compositions and properties of these products were incompatible with the expected structures. In fact, earlier work in our laboratory showed that such reagents degrade the phosphazene skeleton of I in preference to replacement of halogen. Similar ring cleavage reactions have been reported when the cyclic $(NPCl_2)_3$ or 4 interact with Grignard or organolithium reagents.[7,8] However, small molecule fluorocyclophosphazenes, such as $(NPF_2)_{3\text{ or }4}$[9,10] are less susceptible to skeletal cleavage under these conditions, and it was of interest to examine the reactions of high polymeric $(NPF_2)_n$ with organometallic reagents.

We report here that high molecular weight poly(difluorophosphazene) (IV) is a suitable substrate for reaction with some organometallic reagents. The poly(difluorophosphazene) prepared by the published techniques[11,12] is a cross-linked material that is insoluble in all solvents and cannot be used for substitution reactions. We have found that careful, controlled polymerization of highly purified molten $(NPF_2)_3$ (III) at 350° in a high pressure autoclave system for 16-24 hr yielded an elastomeric form of IV that was soluble in organic media. Perfluorodecalin or perfluoro-2-butyltetrahydrofuran are suitable solvents, although the addition of 10 vol % of diethyl ether was sometimes necessary to effect complete solution of the polymer. Crosslinking and insolubilization of IV normally occur after about 50% of the trimer has been polymerized.



The soluble poly(difluorophosphazene) reacted cleanly with aryllithium reagents or with dialkylmagnesium compounds to yield partly substituted, soluble, high molecular weight poly(aryl- or alkylphosphazenes) (V). The remaining fluorine in V was removed by reaction with nucleophiles, such as CF_3CH_2ONa to yield hydrolytically stable, mixed substituent polymers such as VI. Attempts to achieve total replacement of fluorine in IV led to a marked shortening of the chains, although up to 80-90% of the fluorine could be replaced by alkyl or aryl without the polymer incurring a serious decline in molecular weight. The products of these reactions are flexible or elastomeric materials with unusual combinations of physical properties. The following are examples of typical reactions.

Phenyllithium prepared from bromobenzene (26.2 g, 0.17 mol) and excess lithium in diethyl ether (200 ml) was added to a solution of IV (4.6 g, 0.055 mol) in perfluorobutyltetrahydrofuran (175 ml) and diethyl ether (12 ml) as a heterophase suspension in tetrahydrofuran (THF) (1000 ml). After 6 min reaction at 21°, the mixture was treated with a solution prepared from trifluoroethanol (18 ml, 0.25 mol) and sodium (2.1 g, 0.11 mol) in THF (150 ml). After 18 hr reaction at 61°, the polymer was isolated by precipitation in dilute aqueous hydrochloric acid, followed by sequential precipitation from THF into water, acetone, and hexane (yield 41%). The white, flexible, film-forming polymer had a glass transition temperature (Tg) of 60°. Infrared and nmr spectra were compatible with structure VI. ^{31}P nmr spectra showed a peak at +2.16 ppm with a shoulder at +7.69 ppm.[13] Gel permeation chromatography (GPC)[14] suggested a molecular weight near 1.2×10^6. Elemental analysis[15] indicated that 62% of the side groups were phenyl and 38% were CF_3CH_2O. Comparative tests indicated that this polymer showed a greater resistance to molecular weight decline at 300° than did $[NP(OCH_2CF_3)_2]_n$. Prolonged reaction of IV with phenyllithium (for example, for 12 hr at 20°) raised the phenyl side group content to 84%[16], while the molecular weight declined to ≈ 80,000. More vigorous reaction conditions yielded fully substituted[17] but lower molecular weight materials ($\bar{M}_n \approx 2{,}500$)

Similar techniques were employed for the interaction of diethylmagnesium or dibutylmagnesium in THF or glyme with solutions of IV in perfluorobutyltetrahydrofuran. After 2 days reaction with Et_2Mg at 25°, followed by treatment with CF_3CH_2ONa/CH_3CH_2OH at 60° for 24 hr, a highly elastomeric polymer was isolated (yield 20%). It was soluble in THF and chloroform. The $\bar{M}_n$ molecular weight by GPC analysis[14] was 6×10^5, and microanalysis indicated that 90% of the side groups were ethyl and 10% were CF_3CH_2O.[18] ^{31}P nmr analysis showed one peak at -15.99 ppm.[13] The Tg value was -50°.

It is clear that this synthetic method via polymer IV provides a valuble route to the synthesis of a new class of potentially useful macromolecules.

Acknowledgment. We thank the Office of Naval Research for the support of this work.

References and Notes

1. H. R. Allcock and R. L. Kugel, J. Amer. Chem. Soc., 87, 4216 (1965).

2. H. R. Allcock, R. L. Kugel, and K. J. Valan, Inorg. Chem., 5, 1709 (1966).

3. H. R. Allcock and R. L. Kugel, Inorg, Chem., 5, 1716 (1966).

4. For recent summaries of these developments, see H. R. Allcock, Science, 193, 1214 (1976); D. P. Tate, J. Polymer. Sci., Polym. Symp., 48, 33 (1974); R. E. Singler, N. S. Schneider, and G. L. Hagnauer, Polym. Eng. Sci., 15, 321 (1975).

5. C. F. Liu and R. L. Evans, U.S. Patent, 3,169,933 (1965).

6. J. R. MacCallum and J. Tanner, J. Polymer Sci., A1, 6, 3163 (1968).

7. M. Biddlestone and R. A. Shaw, J. Chem. Soc., A, 178 (1968); 1750 (1970).

8. M. Biddlestone and R. A. Shaw, Phosphorus, 3, 95 (1973).

9. C. W. Allen and T. Moeller, Inorg. Chem., 7, 2178 (1968).

10. T. N. Ranganathan, S. M. Todd, and N. L. Paddock, Inorg. Chem., 12, 316 (1973).

11. F. Seel and J. Langer, Angew. Chem., 68, 461 (1956).

12. H. R. Allcock, R. L. Kugel, and E. G. Stroh, Inorg, Chem., 11, 1120 (1972).

13. Relative to aqueous 85% H_3PO_4. The ^{31}P spectrum for $[NP(OCH_2CF_3)_2]_n$ shows a peak at +8.2 ppm.

14. The $\overline{M}_n$ molecular weights were estimated by gel permeation chromatography comparison with polystyrene standards with the use of 10^6 Styragel columns. The solvent was THF.

15. Anal. Calcd. for $[NP(C_6H_4)_{1.24}(OCH_2CF_3)_{0.76}]_n$: C, 49.88; H, 3.58; N, 6.49; P, 14.35; F, 20.07. Found: C, 50.20; H, 3.55; N, 6.43; P, 14.30; F, 19.60.

16. Anal. Calcd. for $[NP(C_6H_4)_{1.68}(F)_{0.32}]_n$: C, 67.00; H, 4.65; N, 7.76; P, 17.20; F, 3.37. Found: C, 66.87; H, 4.70; N, 7.67; P, 17.02; F, 3.40.

17. Anal. Calcd. for $[NP(C_6H_5)_2]_n$: C, 72.36; H, 5.85; N, 7.03; P, 15.59. Found: C, 71.27; H, 5.85: N, 6.31; P, 16.33.

18. Anal. Calcd. for $[NP(CH_2CH_3)_{1.80}(OCH_2CF_3)_{0.20}]_n$: C, 41.00; H, 8.03; N, 11.97; P, 26.49; F, 9.74. Found: C, 41.80; H, 7.89; N, 11.79; P, 26.35; F, 9.78.

Harry R. Allcock*, Dennis B. Patterson, and Thomas L. Evans
Department of Chemistry, The Pennsylvania State University
University Park, Pennsylvania 16802

TECHNICAL REPORT DISTRIBUTION LIST

	No. Copies
Office of Naval Research Arlington, Virginia 22217 Attn: Code 472	2
Office of Naval Research Arlington, Virginia 22217 Attn: Code 102IP	6
ONR Branch Office 536 S. Clark Street Chicago, Illinois 60605 Attn: Dr. George Sandoz	1
ONR Branch Office 715 Broadway New York, New York 10003 Attn: Scientific Dept.	1
ONR Branch Office 1030 East Green Street Pasadena, California 91106 Attn: Dr. R. J. Marcus	1
ONR Branch Office 760 Market Street, Rm. 447 San Francisco, California 94102 Attn: Dr. P. A. Miller	1
ONR Branch Office 495 Summer Street Boston, Massachusetts 02210 Attn: Dr. L. H. Peebles	1
Director, Naval Research Laboratory Washington, D.C. 20390 Attn: Library, Code 2029 (ONRL) Technical Info. Div. Code 6100, 6170	 6 1 1
The Asst. Secretary of the Navy (R&D) Department of the Navy Room 4E736, Pentagon Washington, D.C. 20350	1
Commander, Naval Air Systems Command Department of the Navy Washington, D.C. 20360 Attn: Code 310C (H. Rosenwasser)	1

	No. Copie
Defense Documentation Center Building 5, Cameron Station Alexandria, Virginia 22314	12
U.S. Army Research Office P.O. Box 12211 Research Triangle Park, North Carolina 27709 Attn: CRD-AA-IP	
Commander Naval Undersea Research & Development Center San Diego, California 92132 Attn: Technical Library, Code 133	1
Naval Weapons Center China Lake, California 93555 Attn: Head, Chemistry Division	1
Naval Civil Engineering Laboratory Port Hueneme, California 93041 Attn: Mr. W. S. Haynes	1
Professor O. Heinz Department of Physics & Chemistry Naval Postgraduate School Monterey, California 93940	1
Dr. A. L. Slafkosky Scientific Advisor Commandant of the Marine Corps (Code RD-1) Washington, D.C. 20380	1
Mr. Michael T. McCracken Room 407, MMCC Carnegie-Mellon University Pittsburgh, Pa. 15213	1
Dr. Robert E. Singler Department of the Army Army Materials and Mechanics Research Center Watertown, Massachusetts 02172	

TECHNICAL REPORT DISTRIBUTION LIST

	No. Copies
Dr. T. C. Williams Union Carbide Corp. Chemicals & Plastics Tarrytown Technical Center Tarrytown, New York 10591	1
Dr. K. A. Reynard Horizons Inc. 23800 Mercantile Road Cleveland, Ohio 44122	1
Dr. R. Soulen, Director Contract Research Department Pennwalt Corp. 900 First Avenue King of Prussia, Pennsylvania 19406	1
Dr. A. G. MacDiarmid University of Pennsylvania Department of Chemistry Philadelphia, Pennsylvania 19174	1
Dr. E. Hedaya Union Carbide Corp. Corporate Research Laboratory Tarrytown,Technical Center Tarrytown, New York 10591	1
Dr. A. Rheingold SUNY Plattsburg Department of Chemistry Plattsburg, New York 12901	1
Dr. C. Pittman University of Alabama Department of Chemistry University, Alabama 35486	1
~~Dr. H. Allcock~~ ~~Pennsylvania State University~~ ~~University Park, Pennsylvania 16802~~	1
Dr. M. Kenney Case-Western University Department of Chemistry Cleveland, Ohio 44106	
Dr. R. Lenz Department of Chemistry University of Massachusetts Amherst, Massachusetts 01002	1

	No. Copies
Dr. M. Good Department of Chemistry University of New Orleans Lakefront New Orleans, Louisiana 70122	1
Douglas Aircraft Co. 3855 Lakewood Boulevard Long Beach, California 90846 Attn: Technical Library Cl 290/36-84 AUTO-Sutton	1
NASA-Lewis Research Center 21000 Brookpark Road Cleveland, Ohio 44135 Attn: Dr. T. T. Serafini, MS 49-1	
Dr. J. Griffith Naval Research Laboratory Chemistry Section, Code 6120 Washington, D.C. 20375	1
Dr. G. Goodman Globe-Union Inc. 5757 North Green Bay Avenue Milwaukee, Wisconsin 53201	1
Dr. E. Fischer, Code 2853 Naval Ship Research and Development Center Annapolis Division Annapolis, Maryland 21402	
Dr. Martin H. Kaufman, Head Materials Research Branch (Code 4542) Naval Weapons Center China Lake, California 93555	
Dr. Selwyn H. Rose DeSoto Inc. Administrative and Research Center 1700 South Mt. Prospect Rd. Des Plaines Illinois 60018	